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(71) Applicant: REGENTS OF THE UNIVERSITY OF MINNESOTA [US/US]; 1100 Washington Avenue, Minneapolis, MN 55415 (US).

(72) Inventors: YOKOYAMA, Chikafumi; University of Minnesota, Amundson Hall, 421 Washington Avenue, S.E., Minneapolis, MN 55455 (US). BHARADWAJ, Sameer, S.; University of Minnesota, Amundson Hall, 421 Washington Avenue, S.E., Minneapolis, MN 55455 (US). SCHMIDT, Lanny, D.; University of Minnesota, Amundson Hall, 421 Washington Avenue, S.E., Minneapolis, MN 55455 (US).

(74) Agent: JOHNSON, Kenneth, H.; P.O. Box 630708, Houston, TX 77263 (US).

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(54) Title: CATALYTIC OXIDATIVE DEHYDROGENATION PROCESS AND CATALYST

(57) Abstract

A process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or mixtures thereof comprising reacting said hydrocarbons and molecular oxygen in the presence of a platinum catalyst. The catalyst consists essentially of platinum modified with Sn or Cu and supported on a ceramic monolith.

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CATALYTIC OXIDATIVE DEHYDROGENATION PROCESS AND CATALYST

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to oxidation/dehydrogenation catalysts and a process for the dehydrogenation of dehydrogenatable hydrocarbons in the presence of the oxidation/dehydrogenation catalysts and an oxygen-containing gas.

The dehydrogenation of hydrocarbons is an important commercial process. This is because of the great demand for dehydrogenated hydrocarbons as feedstocks for industrial processes. For example, dehydrogenated hydrocarbons are utilized in the manufacture of various products such as detergents, high octane gasolines, and pharmaceutical products among others. Plastics and synthetic rubbers are other products which may be produced through use of dehydrogenated hydrocarbons. One example of a specific dehydrogenation process is dehydrogenating isobutane to produce isobutene which may be etherified to produce gasoline octane improvers, polymerized to provide adhesive tackifying agents, viscosity-index additives and plastic anti-oxidants.

Related Art

Various reticulated ceramic structures are described in the art: U.S. Pat. No. 4,251,239 discloses fluted filter of porous ceramic having increased surface area; U.S. Pat. No. 4,568,595 discloses reticulated ceramic foams with a surface having a ceramic sintered coating closing off the cells; U.S. Pat. No. 3,900,646 discloses ceramic foam with a nickel coating followed by platinum deposited in a vapor process; U.S. Pat. No. 3,957,685 discloses nickel or palladium coated on a negative image ceramic metal/ceramic or metal foam; U.S. Pat. No. 3,998,758 discloses ceramic foam with nickel, cobalt or copper deposited in two layers with the second layer reinforced with aluminum, magnesium or zinc; U.S. Pat. Nos. 4,810,685 and 4,863,712 disclose negative image reticulated foam coated with active material, such as, cobalt, nickel or molybdenum coating;

U.S. Pat. No. 4,308,233 discloses a reticulated ceramic foam having an activated alumina coating and a noble metal coating useful as an exhaust gas catalyst; U.S. Pat. No. 4,253,302 discloses a foamed ceramic containing platinum/rhodium catalyst for exhaust gas catalyst; and U.S. Pat. No. 4,088,607 discloses a ceramic foam having an active aluminum oxide layer coated by a noble metal containing composition such as zinc oxide, platinum and palladium.

The supports employed in the present invention are generally of the type disclosed in U.S. Pat. No. 4,810,685 using the appropriate material for the matrix and are generally referred to in the art and herein as "monoliths".

The monoliths with various catalytic materials deposited thereon have also been employed for the production of synthesis gas (PCT WO 90/06279) and nitric acid (U.S. Pat. No. 5,217,939)

U.S. Pat. No. 4,940,826 (Freide, et al) discloses the oxidative dehydrogenation of gaseous paraffinic hydrocarbons having at least two carbon atoms or a mixture thereof by contacting the hydrocarbon with molecular oxygen containing gas over a supported platinum catalyst where the support is alumina such as gamma alumina spheres and monoliths such as cordierite or mullite. The desired products are the corresponding olefins.

Various modifiers are disclosed for the monolith/noble metal. Canadian patent 2,004,219 lists Group IV elements as coating materials for monoliths and U.S. Pat No. 4,927,857 discloses a platinum/monolith partial oxidation catalyst supplemented with copper used in conjunction with a steam reforming process. Neither of these references suggests the use of modified platinum/monolith catalyst in oxidative dehydrogenations.

SUMMARY OF THE INVENTION

Briefly the present invention is a process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or mixtures thereof comprising reacting said hydrocarbons and molecular

oxygen in the presence of a platinum catalyst modified with Sn or Cu, preferably in the substantial absence of Pd and Rh on a monolith support. The catalysts consist essentially of platinum modified with Sn or Cu on a ceramic monolith support, preferably alumina or zirconia monolith support.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows ethane conversion as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

Fig. 2 shows ethylene selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

Fig. 3 shows ethylene yield as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

Fig. 4 shows CO selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

Fig. 5 shows CO_2 selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

Fig. 6 shows H_2 selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

Fig. 7 shows H_2O selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

Fig. 8 plots the conversion of ethane and ethylene selectivity as a function of the ratio of Sn:Pt.

Fig. 9 illustrates the effect of feed preheating on ethane conversion, ethylene selectivity and ethylene yield.

Fig. 10 shows n-butane conversion as a function of the butane:oxygen ratio for Sn and Cu modified Pt monolith.

Fig. 11 shows i-butane conversion as a function of the i-butane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The composition of the ceramic support can be any oxide or combination of oxides that is stable at the high temperatures of operation, near 1000°C. The support material should have a low thermal expansion coefficient. The components of the oxide support should not phase separate at high temperatures since this may lead to loss of integrity. Components of the oxide support should not become volatile at the high reaction temperatures. Suitable oxide supports include the oxides of Al (α-Al_2O_3), Zr, Ca, Mg, Hf, and Ti. Combinations of these can be produced to tailor the heat expansion coefficient to match the expansion coefficient of the reactor housing.

The structure and composition of the support material is of great importance. The support structure affects the flow patterns through the catalyst which in turn affects the transport to and from the catalyst surface and thus the effectiveness of the catalyst. The support structure should be macroporous with 30 to 80 pores per linear inch. The pores should yield a tortuous path for the reactants and products such as is found in foam ceramics. Straight channel extruded ceramic or metal monoliths yield suitable flow dynamics only if the pore size is very small with >80 pores per linear inch.

The preferred catalyst of the present invention consists essentially of platinum modified with Sn or Cu (a mixture of Sn and Cu may be used) supported on a ceramic foam monolith, preferably on zirconia or α-alumina. The platinum should be deposited on the surface of the ceramic to a loading of 0.2 to 90 wt. %, preferably 2 to 10 wt. %, and more preferably in the absence or substantial absence of palladium, rhodium, and gold. It has been found that palladium causes the catalyst to coke up and deactivate very quickly and thus should be excluded in any amount that is detrimental to the effectiveness of the catalyst. Though rhodium does not lead to catalyst deactivation the product distribution is less favorable.

Preferably the Pt and modifying Sn or Cu is supported

on an α-alumina or zirconia ceramic foam monolith with 30 to 80 pores per linear inch, 50 to 90% void fraction, created in such a way to yield a tortuous path for reactants. The Pt and modifiers may be supported on a ceramic foam monolith comprised of any combination of α-alumina, zirconia, titania, magnesia, calcium oxide, or halfnium oxide such that the support is stable up to 1100°C and does not undergo detrimental phase separation that leads to loss in catalyst integrity.

In addition to Sn and Cu, several other metals were evaluated as modifiers. Pt/Ag exhibited comparable conversion and C_2H_4 selectivity to Pt alone. Experiments using Ag were identical to those described below but experiments were less extensive for poor catalysts (Pt/Mg, Pt/Ce, Pt/Ni, Pt/La, Pt/Co). The addition of the other metals lowered both conversion and olefin selectivity in the order of Sn > Cu > Pt alone > Ag > Mg > Ce > Ni > La > Co as demonstrated with ethane. With lower C_2H_4 selectivity, syngas ($CO+H_2$) formation became predominant. Pt/Au could not be ignited with $C_2H_6+O_2$. NH_3 and O_2 were used for light-off of the Pt/Au catalyst, however, the catalyst extinguished quickly when C_2H_6 was introduced in spite of the presence of NH_3. The results on the catalysts containing the various metals were summarized in Table I.

TABLE I

Comparison of Metals

Catalyst	Atomic ratio (Metal:Pt)	Reaction temp °C	Conv. of C_2H_6 %	S_{C2H_4} %	S_{COx} %	Y_{C2H_4} %	Max. Y_{C2H_4} (at C_2H_6:O_2)
Pt	0	920	69.7	64.9	26.9	45.3	52.7 (1.5)
Pt/Sn	1	912	71.5	68.2	24.1	48.8	55.3 (1.5)
Pt/Sn	3	905	72.8	68.0	24.4	49.5	55.4 (1.5)
Pt/SN	7	920	75.7	69.0	21.9	52.3	57.4 (1.7)
Pt/Cu	1	928	74.4	68.1	23.8	50.7	55.0 (1.7)
Pt/Cu	3	extinguished in C_2H_6+O_2					
Pt/Ag	1		62.6	64.3	26.4	40.2	51.6 (1.7)
Pt/Mg	3	943	65.1	60.6	33.6	39.5	43.4 (1.7)
Pt/Ce	3	905	60.2	49.7	47.7	29.9	31.2 (1.7)
Pt/La	3	905	56.0	41.7	56.0	23.4	24.8 (1.7)
Pt/Ni	1	905	58.7	46.3	50.4	27.2	29.3 (1.7)
Pt/Co	1	873	50.8	26.8	71.4	13.1	15.3 (1.7)
Pt/Au	1	extinguished in C_2H_6+O_2					

Note. All conversions, selectivities, and temperatures at C_2H_6:O_2=1.9 and 5 slpm without preheat. Pt loadings of all catalysts are wt%.

The paraffins which are suitable for the present process are generally those that can be vaporized at temperatures in the range of 25 to 400°C at pressures of 0.1 to 5 atm. These are generally C_2 to C_{20} carbon atom alkanes either alone or in mixtures, preferably having two to eight carbon atoms. Suitable alkanes include ethane, propane, n-butane isobutane, n-pentane, isoamylenes, n-hexane, isohexanes, n-heptane, isoheptane, octane and isooctanes. Since a preferred embodiment includes a preheating of the feed to the reaction zone, the necessity to heat an alkane feed above ambient temperature to obtain a vaporous feed is not a negative consideration.

The feed may include both linear and branched alkanes. It has been observed in a fuel rich regime for the oxidative dehydrogenation of n-butane that the oxygen is completely consumed, whereas for the isobutane oxidations it is not. This oxygen breakthrough suggests a rate limiting step for isobutane. It is a proposed theory that the rates of these reactions should be related to the strengths of C-H bonds that must be broken. Thus, it may be desirable to preheat those feeds which are determined to have relatively strong C-H bonds to increase the rate of the initiation step. The feeds may be preheated to temperatures in the range of 0 to 500°C., preferably 25 to 400°C.

The present invention discloses the catalytic oxidative dehydrogenation of hydrocarbons. Mixtures of hydrocarbons and oxygen are flammable between given compositions. The feed compositions cited in this invention are outside the flammability limits for the cited hydrocarbons. In all cases, the feed compositions are on the fuel-rich side of the upper flammability limit. The compositions range from 2 to 16 times the stoichiometric fuel to oxygen ratios for combustion to CO_2 and H_2O. Some molar ratios are set out below in Table II.

TABLE II

Fuel	Operable Fuel: oxygen molar ratio	Preferred Fuel: oxygen molar ratio
Ethane	0.8-2.5	1.5-2.0
Propane	0.5-1.5	0.8-1.3
n-Butane	0.45-1.0	0.6-0.8
i-Butane	0.45-2.25	1.4-2.1

As the diluent is reduced and as the reactants are preheated, the flammability limits widen, but it is under these conditions that higher fuel to oxygen ratios (farther from the flammable range) are preferred. This preference is based on catalyst performance with the extra measure of safety an added benefit.

Under the conditions of the present process, olefin cracking, CO disproportionation and reverse steam reforming of carbon can occur, and may lead to coke formation. It has been found by varying the catalyst contact time, the amount of time allowed for these secondary reactions can be controlled. At higher flow rates the olefin products spend less time in contact with the catalyst and higher olefin selectivities and less coking are observed.

The present invention discloses the catalytic oxidative dehydrogenation of hydrocarbons in an autothermal reactor at millisecond contact time. High yields of mono-olefins are obtained with a catalyst contact time ranging from 0.1 to 20 milliseconds when using a ceramic foam monolith of 50 to 90% porosity and 0.2 to 1 cm in depth. Under operating conditions, this corresponds to GHSV of 60,000 to 3,000,000 hr^{-1}.

The flow rates are in the range of 60,000-10,000,000 hr^{-1} GHSV, preferably in the range of 300,000 up to 3,000,000 hr^{-1} GHSV may be used.

Under the conditions of the present process it can be determined that several reactions may occur namely (1) complete combustion (strongly exothermic); (2) partial oxidation to syngas (exothermic); (3) oxidative

dehydrogenation (exothermic); (4) dehydrogenation (endothermic) and cracking (endothermic).

The overall process can be carried out autothermally. The heat produced by exothermic reactions provides the heat for endothermic reactions. The process does not require the addition of heat.

However, improved results are obtained when moderate amounts of heat are supplied to the system. Preheating the feed shifts the product distribution from the more exothermic reactions (combustion and partial oxidation) to the less exothermic (oxidative dehydrogenation) and endothermic (dehydrogenation and cracking) reactions. Since oxygen is the limiting reactant, this shift improves the process conversion. The selectivity is improved since the less exothermic and endothermic reactions are the desired reactions.

EXAMPLES

The reactor used in the following examples consisted of a quartz tube with an inside diameter of 18 mm containing the catalytic monolith which was sealed into the tube with high temperature alumina-silica cloth that prevented bypass of the reactant gases around the edges of the catalyst. To reduce radiation heat loss and better approximate adiabatic operation, the catalyst was immediately preceded and followed by inert alumina extruded monolith heat shields. The outside of the tube near the reaction zone was insulated.

The Pt/M (M=Sn, Cu, Ag, Mg, Ce, La, Ni, Co, and Au) bimetallic catalysts were prepared as follows: First, Pt was added to α-Al_2O_3 foam monoliths (17 mm diameter x 10 mm long, 45 pores per inch (ppi) by impregnation with aqueous solutions of H_2PtCl_6. The samples were dried in vacuum at room temperature, followed by calcination at 100°C for 0.5 hr. and at 350° for 2 hrs. in oxygen. The second metal was then added by impregnation with aqueous solutions of corresponding metal salts: $SnCl_2$, $Cu(NO_3)_2$, $AgNO_3$, $Mg(NO_3)_2$, $Ce(NO_3)_3$, $La(NO_3)_3$, $Ni(OOCCH_3)_2$, $Co(OOCCH_3)_2$, and $AuCl_3$. The Pt/M monoliths were then dried in vacuum at

room temperature, calcined at 100°C for 0.5 hr and at 700°C for 1.5 hrs. in oxygen, and then reduced at 700°C for 1.5 hr. in hydrogen. Pt loadings of all samples were either 2 or 5 wt%. The other metal loadings are summarized in Table 1.

The catalysts are prepared by depositing Pt, a mixture of components or components sequentially on commercially available ceramic foam monoliths. The foam monoliths, available from Hi-Tech Ceramics, Inc., are composed of either α-Al_2O_3 or ZrO_2 with 30, 45 or 80 pores per linear inch (ppi). It is important to note that these catalysts are not microporous structures. The monoliths are not wash-coated and are estimated to have a surface area of less than 70 cm^2/g. Suitable catalysts contain 0.2 to 20 wt% Pt and tin in an atomic ratio to Pt of 0.5 to 7:1 or copper in an atomic ratio to Pt of 0.5 to <3:1.

Gas flow into the reactor was controlled by mass flow controllers which had an accuracy of $\pm$ 0.1 slpm for all gases. The feed flow rates ranged from 5 slpm total flow, corresponding to 37 cm/s superficial velocity (i.e. the velocity of the feed gases upstream from the catalyst, approximately 250 cm/s in the monolith at reaction conditions) at room temperature and atmospheric pressure. For ethane oxidation the ethane:oxygen ratio was varied from 1.5 to 2.1 at a fixed nitrogen dilution (30%). For butane oxidation, the butane:oxygen ratio was changed from 0.8 to 1.4 at 50% nitrogen. In all runs, the reactor pressure was maintained at 1.4 atm. The runs were carried out with O_2 as the oxidant. N_2 was typically added at a percent of the feed as an internal GC calibration standard. The reaction temperature was ≈1000°C and contact times were from 0.2 to 40 msec. Product gases were fed through heated stainless steel lines to an automated gas chromatograph. Shutdown of the reactor was accomplished by turning off oxygen before alkane.

The product gases were analyzed by a gas chromatograph equipped with a single Hayesep DB packed column. For quantitative determination of concentrations, standards

were used for all species except for H_2O, which was obtained most reliably from an oxygen atom balance. Nitrogen was used as an internal GC calibration standard. The selectivity data shown was calculated on a carbon atom or a hydrogen atom basis, as described below.

To convert the product gas concentrations to molar quantities for a given feed basis, the mole number change due to the chemical reactions was calculated using the measured N_2 concentration. Since N_2 is an inert in this system, the ratio of product gas to feed gas moles was inversely proportional to the ratio of product gas N_2 concentration to feed gas N_2 concentration. Individual species concentrations were measured with a reproducibility estimated to be $\pm 2\%$.

Temperatures were monitored using thermocouples inserted from the rear of the quartz tube in one of the center channels of the inert monolith immediately after the catalytic monolith. The reactor was operated at a steady state temperature which is a function of the heat generated by the exothermic and endothermic reactions and the heat losses from the reactor.

Although the process in steady state is autothermal with feed gases at room temperature, heat was supplied initially to ignite the reaction. A mixture of hydrocarbon and air near the stoichiometric composition for production of synthesis gas was fed to the reactor, and the reactants were heated to the heterogeneous ignition temperature (≈230°C for C_2 to C_4 hydrocarbons). After light-off, the external heat source was removed (unless feed preheating is indicated), the reaction parameters were adjusted to the desired conditions, and steady state was established (≈10 min) before analysis. For situations where the catalyst was not ignited with a mixture of alkane and oxygen, e.g. Ag as a modifier, a NH_3/O_2 was used for light-off and NH_3 was then gradually exchanged for the alkane. Data shown

were reproducible for time periods of at least several hours and on several catalyst samples.

For C_2H_6 oxidation, the major products over all catalysts were C_2H_4, CO, CO_2, CH_4, H_2, and H_2O. Traces of C_2H_2, C_3H_6, C_3H_8, and C_4H_8 were observed, usually with selectivities < 2%. The conversions of oxygen were always above 97%, so reactions always go to completion.

EXAMPLE 1

Ethane

Pt, Pt/Sn and Pt/Cu Catalysts

Figs. 1, 2, and 3 show the C_2H_6 conversion, C_2H_4 selectivity, and C_2H_4 yield for oxidative dehydrogenation of ethane over Pt, Pt/Sn (Sn:Pt=7:1), and Pt/Cu (Cu:Pt= 1:1) as a function of the feed composition (2.0 is the ethylene stoichiometric ratio). With increasing feed composition, the conversion decreased while the selectivity increased over the three catalysts. The addition of Sn significantly enhanced both the conversion (by ≈7%) and the selectivity (by ≈5%), which produced the highest C_2H_4 yield of 57% at 25°C feed in this study. The Pt/Cu also showed higher conversion and higher selectivity than Pt, the maximum yield being 55%. As shown in Figs. 4, 5, 6 and 7, both Pt/Sn and Pt/Cu showed 5 ≈9% lower CO selectivity and 1 ≈2% higher CO_2 selectivity than Pt. Among minor products, more C_2H_2 and C_4H_8 were formed on both Pt/Sn and Pt/Cu than on Pt. The addition of Sn or Cu inhibited CO production and promoted the formation of olefins and acetylene without significant change in CH_4 selectivities.

The reaction temperatures decreased from 1000 to 900°C as the C_2H_6:O_2 ratio increased from 1.5 to 2.1 and temperatures were same to within ± 20°C on these three catalysts.

No deactivation or volatilization of the catalysts were observed for several hours. No significant coke formation on the catalysts was observed.

EXAMPLE 2

Ethane

Loadings of Pt, Sn, and Cu

Fig. 8 shows plots of C_2H_6 conversion and C_2H_4 selectivity as functions of Sn:Pt ratio at a feed near the oxidative dehydrogenation stoichiometry (C_2H_6:O_2=1.9). The conversion increased with increased Sn:Pt ratio. On the other hand, the addition of a small amount of Sn (Sn:Pt =1:1) enhanced the selectivity significantly and the further addition led to a slight increase in the selectivity.

Pt/Cu (Cu:Pt=1:1) showed comparable results to Pt:Sn, as described above. However, Pt/Cu (Cu:Pt=3:1) could not be ignited in the mixture of C_2H_6 and O_2. A NH_3:O_2 mixture was used for ignition, but the catalyst extinguished upon exchange of NH_3 for C_2H_6,

A sample of 5 wt% Pt was nearly identical to 2 wt% Pt, although the C_2H_6 conversion was 1% lower with 5 wt% loading. The addition of Sn to 5 wt% Pt also enhanced both the conversion and C_2H_4 selectivity. The 5 wt% Pt/Sn (Sn:Pt=1:1) exhibited comparable results (1% higher conversion and 1% lower selectivity to 2 wt% Pt/Sn (Sn:Pt= 1:1). This fact confirms that Sn acts as a promoter for ethane oxidation, regardless of Pt loadings. Neither 5 wt% Pt/Cu (Cu:Pt=1:1) the 2 wt% Pt/Cu (Cu:Pt=3:1) worked autothermally.

EXAMPLE 3

Preheat

Fig. 9 shows the effect of preheat on the conversion, selectivity, and yield over Pt/Sn (7:1) catalyst at C_2H_6:O_2=1.9. Preheat of reaction gases up to 400°C increased the conversion from 77 to 89% and decreased the selectivity from 69 to 65%, which led to an increase in yield from 53 to 58%.

EXAMPLE 4

n-Butane

Oxidative dehydrogenation of n-butane was examined over Pt, Pt/Sn (Sn:Pt=3), and Pt/Cu (Cu:Pt=1). Both Pt/Sn and

Pt/Cu showed much higher C_4H_{10} conversion (by ≈16%) than Pt as a function of feed composition (Fig. 10). On the three catalysts, the selectivities to C_2H_4 and CO_x decreased and selectivity to C_3H_6 increased with increasing C_4H_{10}:O_2 ratio. The C_4H_8 selectivity was only 3-5% and increased slightly with increasing C_4H_{10}:O_2 ratio. The C_2H_4 selectivity from n-C_4H_{10} was much higher on Pt/Sn and Pt/Cu than on Pt, while the C_3H_6 selectivity was much lower on Pt/Sn and Pt/Cu than on Pt.

EXAMPLE 5

i-Butane

Oxidation of i-butane was similar to n-butane. Both Pt/Sn (Sn:Pt=3) and Pt/Cu (Cu:Pt=1) showed much higher conversion (by 15-25%) than Pt (Fig. 11). With i-C_4H_{10} the dominant olefins are i-C_4H_8 (≈30%) and C_3H_6 (≈30%). On all three catalysts, selectivities to C_2H_4 decreased and selectivities to C_3H_6 and i-C_4H_8 increased with increasing C_4H_{10}:O_2 ratio. As a function of conversion, Pt/Sn and Pt/Cu exhibited higher selectivities to olefins and acetylene than Pt at high conversion.

XRD

X-ray diffraction patterns were determined for Pt and Pt/Sn (Sn:Pt=1:1 and 7:1) catalysts after reaction. On Pt catalyst, only peaks of Pt metal were observed except for that of the α-Al_2O_3 support. On the other hand, only PtSn and Pt_3Sn peaks were observed for Pt/Sn catalysts and there were no Pt metal peaks. The PtSn:Pt_3Sn ratio was higher for Pt:Sn (1:7) than for Pt:Sn (1:1). These results clearly indicate that Pt exists in the forms of only Pt_3Sn and PtSn alloys on support for Pt/Sn catalyst.

The addition of Sn or Cu to Pt-monolith enhanced alkane conversion and olefin selectivities and suppressed CO_x formation for the oxidative dehydrogenation reactions. Since Pt exists in the forms of only PtSn and Pt_3Sn alloys on Pt/Sn catalyst, it is speculated that PtSn and Pt_3Sn alloys are the active sites and are more selective to C_2H_4 formation that Pt.

The invention claimed is:

1. A process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or mixtures thereof comprising reacting said hydrocarbons and molecular oxygen in the presence of a platinum catalyst consisting essentially of platinum modified with Sn, Cu or mixtures thereof and supported on a ceramic monolith.

2. The process according to claim 1 wherein the support is alumina monolith.

3. The process according to claim 1 wherein the support is zirconia monolith.

4. The process according to claim 1 wherein the palladium and rhodium are substantially absent.

5. The process according to claim 1 wherein tin is present in an atomic ratio to platinum of 0.5-7:1.

6. The process according to claim 1 wherein copper is present in an atomic ratio to platinum of 0.5-<3:1.

7. The process according to claim 1 wherein said gaseous paraffin and said oxygen have a flow rate in the range of 60,000 to 10,000,000 hr^{-1} GHSV.

8. The process according to claim 7 wherein said gaseous paraffin and said oxygen have a flow rate in the range of 300,000 to 3,000,000 hr^{-1} GHSV.

9. The process according to claim 1 wherein said gaseous paraffinic hydrocarbon comprises an alkane or mixture of alkanes having two to twenty carbon atoms.

10. The process according to claim 9 wherein said alkane or mixture of alkanes have two to eight carbon atoms.

11. The process according to claim 9 wherein said alkane or mixture of alkanes is ethane, propane, n-butane isobutane, n-pentane, isoamylenes, n-hexane, isohexanes, n-heptane, isoheptane, octane, isooctanes or mixtures thereof.

12. The process according to claim 9 wherein said alkane or mixture of alkanes comprises ethane.

13. The process according to claim 9 wherein said

alkane or mixture of alkanes comprises propane.

14. The process according to claim 9 wherein said alkane or mixture of alkanes comprises n-butane.

15. The process according to claim 9 wherein said alkane or mixture of alkanes comprises isobutane.

16. The process according to claim 1 wherein said paraffinic hydrocarbon and molecular oxygen is preheated prior to reacting.

17. The process according to claim 15 wherein said preheating is to a temperature in the range of 25 to 400°C.

18. A process for the production of corresponding olefins, comprising feeding a gaseous alkane or mixture of alkanes having two to twenty carbon atoms and molecular oxygen at a flow rate of 60,000 to 3,000,000 hr^{-1} to a catalyst consisting essentially of platinum 0.2 to 20 wt% and tin in an atomic ratio to Pt of 0.5-7:1 or copper in an atomic ratio to Pt of 0.5-<3:1 supported on a ceramic monolith.

19. A catalyst composition for oxidative dehydrogenations consisting essentially of Pt and Sn, Cu or mixtures thereof in a modifying effective amount.

20. The catalyst according to claim 19 wherein Sn is present.

21. The catalyst according to claim 19 wherein Cu is present.

22. The catalyst according to claim 19 having an atomic ratio of 0.5:1 to 7:1 Sn or 0.5 to <3.0:1 Cu to Pt, said Pt and mixtures with Sn and/or Cu being deposited on a monolith.

23. The catalyst according to claim 19 wherein said monolith comprises ceramic.

24. The catalyst according to claim 19 wherein said monolith comprises oxides of Al, Zr, Ca, mg, Hf or Ti.

25. The catalyst according to claim 19 where Cu is present in an atomic ratio of 0.5 to <3:1 Cu to Pt and Sn is present in an atomic ratio of 0.5 to 7:1 Sn to Pt.

26. The catalyst according to claim 19 wherein said Pt and Cu and/or Sn are co-deposited on said monolith.

27. The catalyst according to claim 19 wherein said Pt and Cu or Sn are sequentially deposited on said monolith.

28. The catalyst according to claim 19 wherein said monolith has a surface area of less than 70 m^2/g and has 30 to 80 pores per linear inch.

29. A catalyst composition according to claim 19 consisting essentially of Pt, and Cu deposited over a zirconia monolith having 30 to 80 pores per linear inch and less than 70 m^2/g surface area.

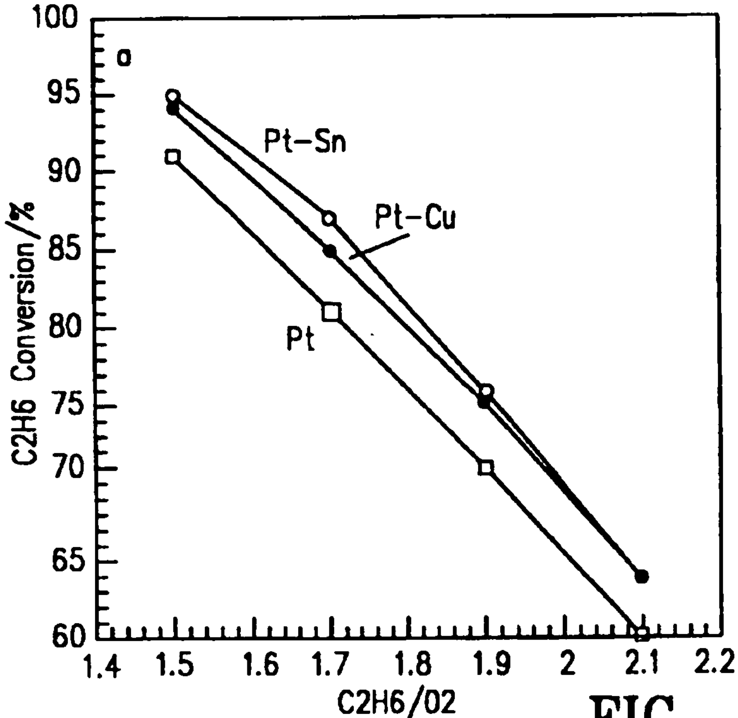
30. A catalyst composition according to claim 19 consisting essentially of Pt, and Cu deposited over an alumina monolith having 30 to 80 pores per linear inch and less than 70 m^2/g surface area.

31. A catalyst composition according to claim 19 consisting essentially of Pt, and Sn deposited over a zirconia monolith having 30 to 80 pores per linear inch and less than 70 m^2/g surface area.

32. A catalyst composition according to claim 19 consisting essentially of Pt, and Sn deposited over an alumina monolith having 30 to 80 pores per linear inch and less than 70 m^2/g surface area.

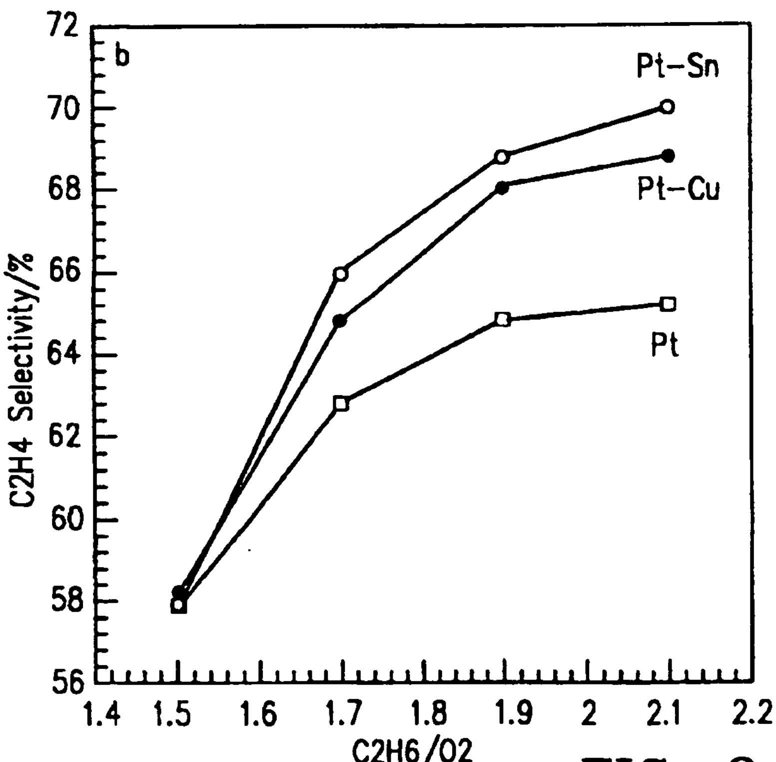
33. A catalyst composition according to claim 19 consisting essentially of Pt, Cu and Sn deposited over a zirconia monolith having 30 to 80 pores per linear inch and less than 70 m^2/g surface area.

34. A catalyst composition according to claim 19 consisting essentially of Pt, Cu and Sn deposited over an alumina monolith having 30 to 80 pores per linear inch and less than 70 m^2/g surface area.



a
100
95
90
85
80
75
70
65
60
C2H6 Conversion/%
Pt-Sn
Pt-Cu
Pt
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
C2H6/O2

FIG. 1



b
72
70
68
66
64
62
60
58
56
C2H4 Selectivity/%
Pt-Sn
Pt-Cu
Pt
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
C2H6/O2

FIG. 2

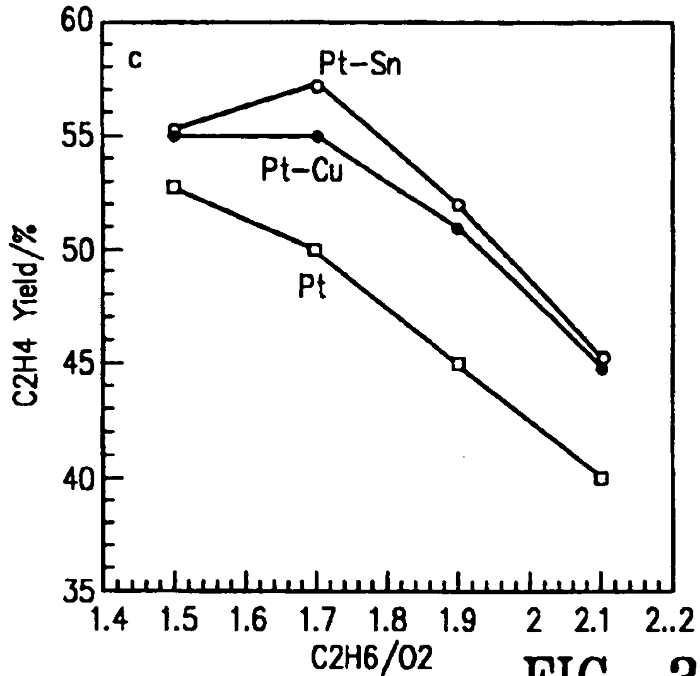

c
Pt-Sn
Pt-Cu
Pt
C2H4 Yield/%
60
55
50
45
40
35
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2..2
C2H6/O2

FIG. 3

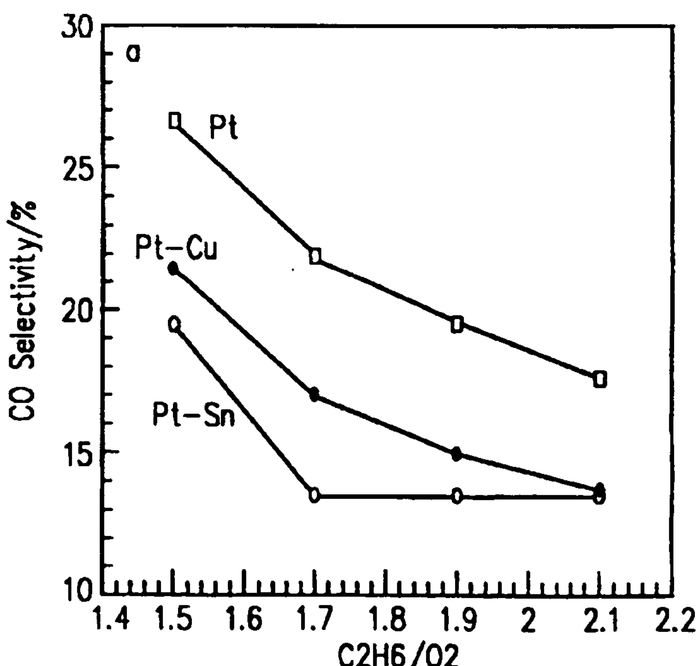

a
Pt
Pt-Cu
Pt-Sn
CO Selectivity/%
30
25
20
15
10
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
C2H6/O2

FIG. 4

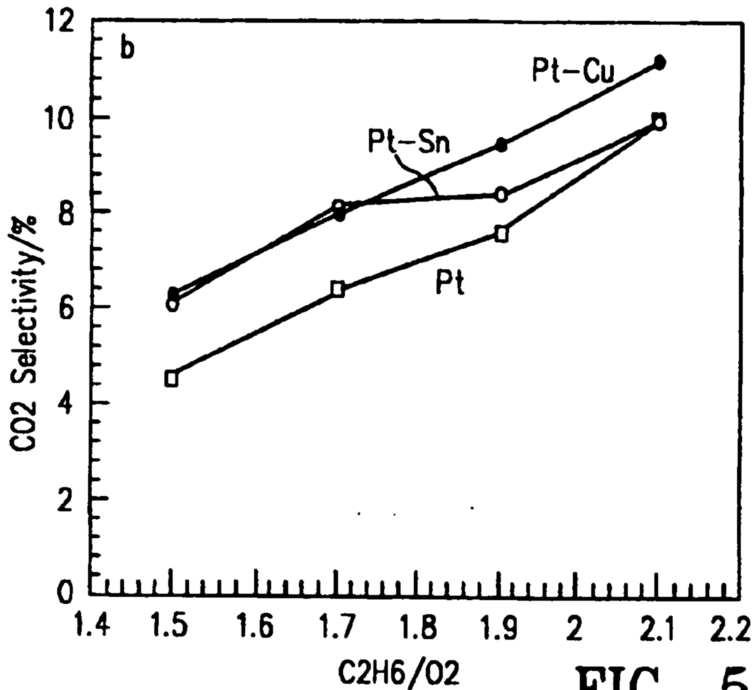

12
10
8
6
4
2
0
b
Pt-Cu
Pt-Sn
Pt
CO2 Selectivity/%
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
C2H6/O2

FIG. 5

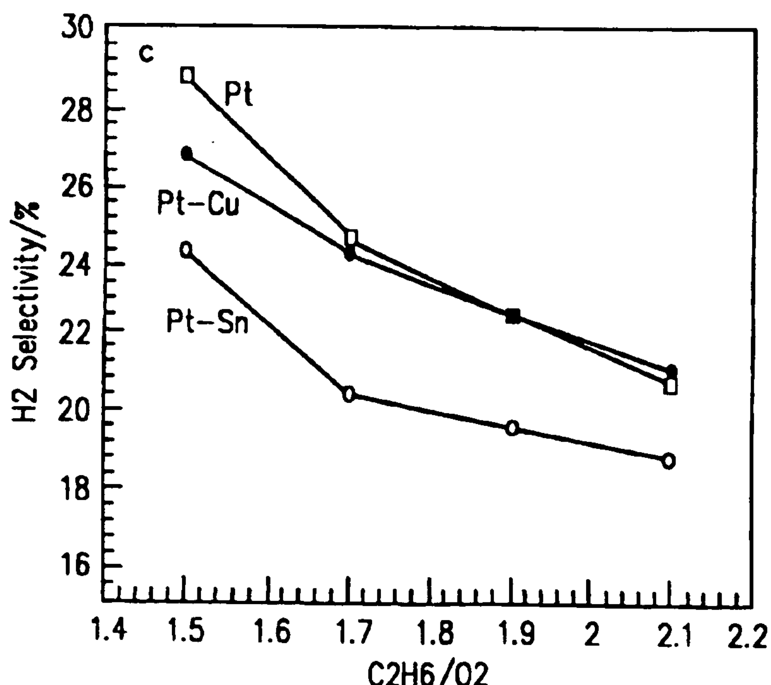

30
28
26
24
22
20
18
16
c
Pt
Pt-Cu
Pt-Sn
H2 Selectivity/%
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
C2H6/O2

FIG. 6

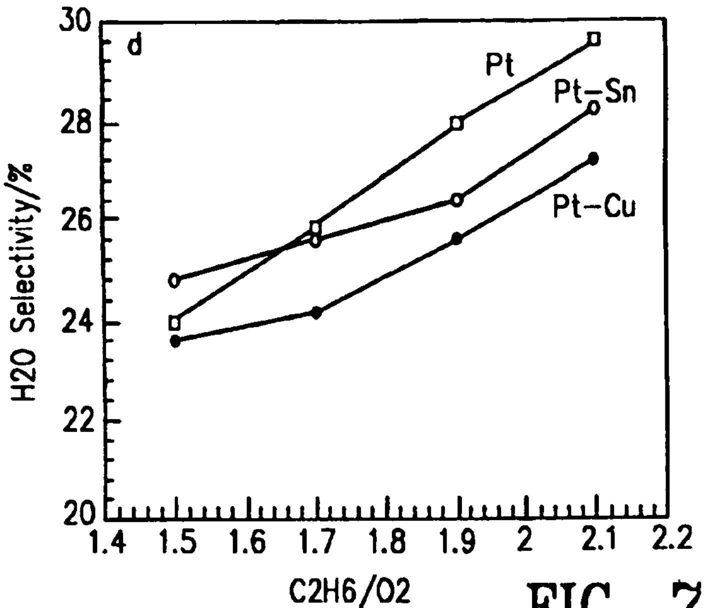

d
Pt
Pt-Sn
Pt-Cu
H2O Selectivity/%
30
28
26
24
22
20
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
C2H6/O2

FIG. 7

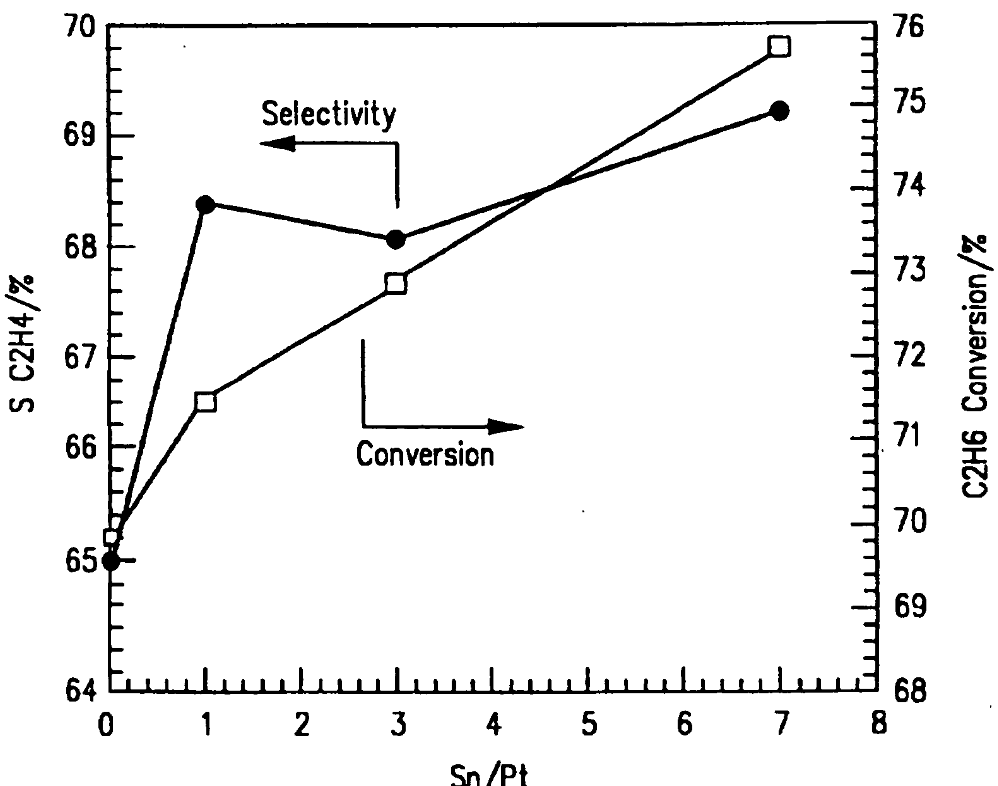

Selectivity
Conversion
S C2H4/%
C2H6 Conversion/%
70
69
68
67
66
65
64
76
75
74
73
72
71
70
69
68
0
1
2
3
4
5
6
7
8
Sn/Pt

FIG. 8

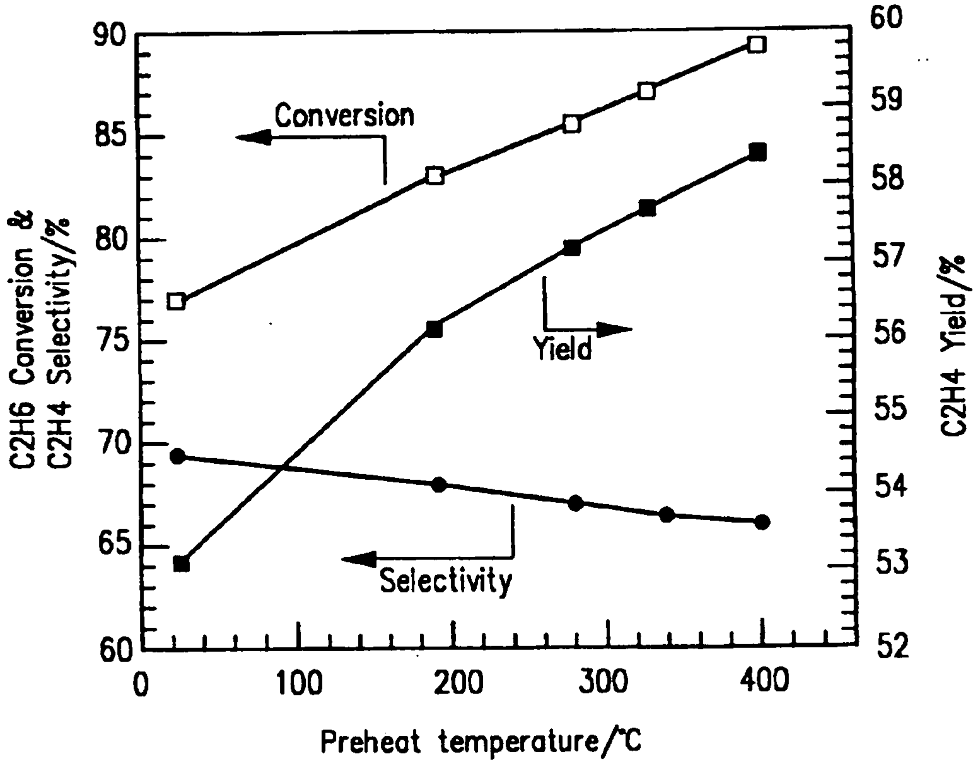

Conversion
Yield
Selectivity
C2H6 Conversion &
C2H4 Selectivity/%
C2H4 Yield/%
Preheat temperature/°C
90
85
80
75
70
65
60
60
59
58
57
56
55
54
53
52
0
100
200
300
400

FIG. 9

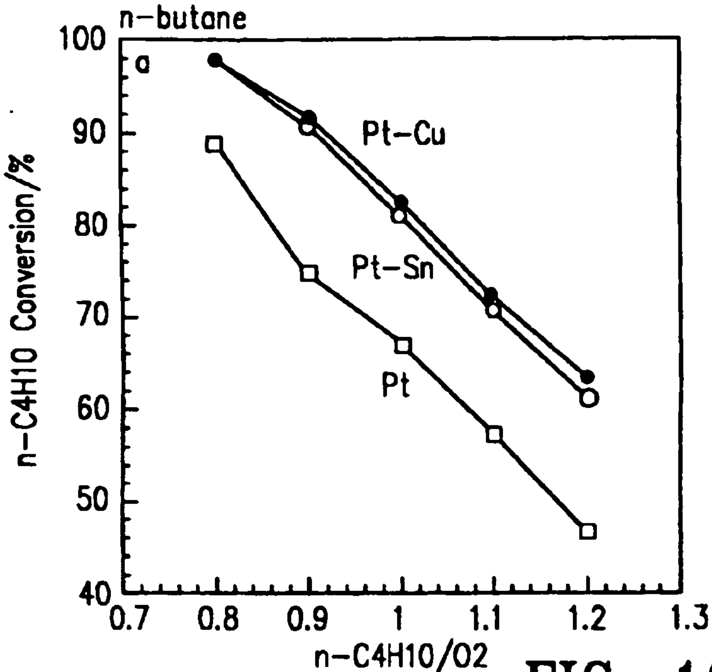

n-butane
a
Pt-Cu
Pt-Sn
Pt
n-C4H10 Conversion/%
n-C4H10/O2
100
90
80
70
60
50
40
0.7
0.8
0.9
1
1.1
1.2
1.3

FIG. 10

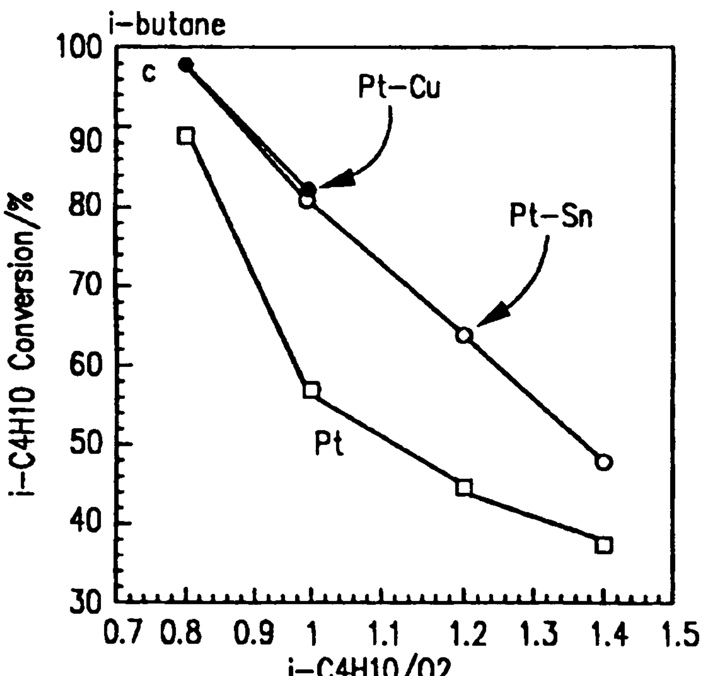

i-butane
c
Pt-Cu
Pt-Sn
Pt
i-C4H10 Conversion/%
i-C4H10/O2
100
90
80
70
60
50
40
30
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5

FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/00548

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 23/00, 23/02, 23/04, 23/58, 23/70; C07C 5/327, 5/333, 5/373
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/325, 330, 331, 344, 345, 349, 351; 585/654, 656, 658, 660, 661

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	US 4,931,419 A (BLANCHARD ET AL.), 05 June 1990, see column 3, lines 31-62.	19-34
A	US 5,413,984 A (MARECOT ET AL.), 09 may 1995, see the entire document.	All

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 FEBRUARY 1997	08 MAY 1997

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ELIZABETH D. WOOD
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

502/325, 330, 331, 344, 345, 349, 351; 585/654, 656, 658, 660, 661